

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-340466

(43)Date of publication of application : 08.12.2000

(51)Int.Cl.

H01G 9/04  
H01G 9/00

(21)Application number : 11-149626

(71)Applicant : HITACHI AIC INC

(22)Date of filing : 28.05.1999

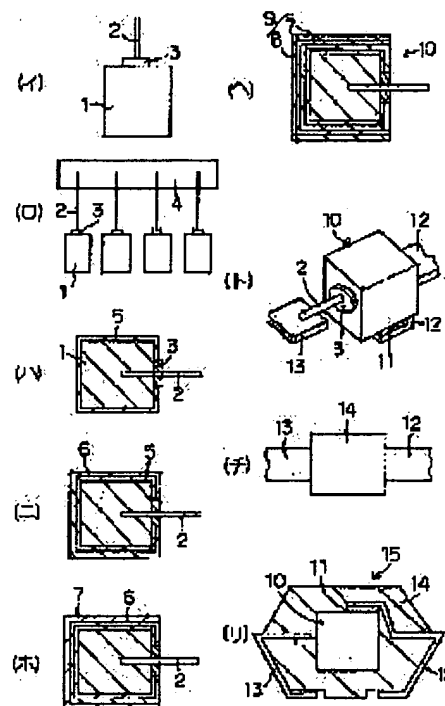
(72)Inventor : TSUNESUMI YASUHIRO  
IIDA KAZUYUKI  
SANO SHINJI

## (54) MANUFACTURE OF SOLID ELECTROLYTIC CAPACITOR

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide the manufacturing method of a solid electrolytic capacitor having improved leakage current characteristics and high reliability.

**SOLUTION:** In the manufacturing process of a solid electrolytic capacitor 15, a capacitor element 10 comprising a sintered unit 1 made of valve-action metal, an oxide film 5 formed on the sintered unit 1, a conductive polymer layer 6 formed on the oxide film 5 and a cathode layer 9 formed on the conductive polymer layer 6 is covered with a covering layer 14 made of resin and subjected to an aging treatment which includes a 1st aging treatment in which a voltage not lower than a rated voltage is applied at a room temperature and a 2nd aging treatment in which a voltage not lower than the rated voltage is applied in a high temperature atmosphere.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of

rejection]

[Kind of final disposal of application other than  
the examiner's decision of rejection or  
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

**\* NOTICES \***

**JPO and INPIT are not responsible for any**

**damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the manufacture approach of a solid electrolytic capacitor of having the layer which consists of conductive polymers, such as the poly aniline and polypyrrole, about the manufacture approach of a solid electrolytic capacitor.

[0002]

[Description of the Prior Art] Solid electrolytic capacitors, such as an tantalum solid electrolytic capacitor, are manufactured by the approach as follows. That is, the end of the lead wire for anode plates which consists of valve action metals, such as a \*\*\*\* tantalum, first is embedded, and press pressurization molding of the powder which mixed the binder to the impalpable powder of valve action metals, such as a tantalum and aluminum, is carried out. After molding and into a vacuum, it heats and sinters by high temperature and a sintered compact is formed. next, this sintered compact -- formation -- into liquid, chemical conversion is immersed and carried out and an oxide film is formed. The layer which consists of conductive polymers, such as a manganese-dioxide layer or polypyrrole, and the poly aniline, is formed after forming an oxide film. Then, sequential formation of a carbon layer and the silver larer is carried out, and it considers as catholyte. And a cathode terminal is connected to a silver larer while connecting an anode terminal to the lead wire for anode plates. Furthermore, some of the capacitor element after forming a silver larer and anode terminals and cathode terminals are covered with sheathing which consists of insulating resin etc. Aging processing is carried out into [ after forming sheathing ] a high temperature ambient atmosphere 85 degrees C or more. And since matter, such as polypyrrole, has high conductivity, the solid electrolytic capacitor which has the layer which consists of conductive polymers, such as poly PIORU, has the description that equivalent series resistance and an impedance are low.

[0003]

[Problem(s) to be Solved by the Invention] By the way, in case a solid electrolytic capacitor forms sheathing which consists of resin, resin contracts and it requires mechanical stress for a manganese-dioxide layer or a conductive polymer layer. And the solid electrolytic capacitor in which especially the conductive polymer layer was formed has the fault in which the leakage current tends to increase for said stress as compared with the solid electrolytic capacitor in which the manganese-dioxide layer was formed.

[0004] This invention improves the above fault, improves a leakage current property, falls a defect, and makes it a technical problem to offer the manufacture approach of a reliable solid electrolytic capacitor.

[0005]

[Means for Solving the Problem] An oxide film is formed in the sintered compact which consists of a valve action metal in order that this invention may solve the above-mentioned technical problem. In the manufacture approach of the solid electrolytic capacitor which forms sheathing which becomes the capacitor element which carried out the laminating of a conductive polymer layer and the catholyte to this oxide film one by one from resin, and carries out aging processing after that The electrical potential difference more than rated voltage is impressed in ordinary temperature, 1st aging processing is carried out, the electrical potential difference more than rated voltage is impressed in the ambient atmosphere of high temperature after that, and the 2nd carries out aging processing.

[0006] That is, according to this invention, the electrical potential difference more than rated voltage is impressed in ordinary temperature, 1st aging processing is carried out, the electrical potential difference more than rated voltage is impressed in the ambient atmosphere of high temperature after that, 2nd by carrying out aging processing, a leakage current property can be improved and dependability can be improved.

[0007]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained. First, the binder which melted camphor, acrylic resin, etc. by the organic solvent is added to the impalpable powder of valve action metals, such as a tantalum, and aluminum, niobium, and it mixes to it. After mixing, it heats, and it volatilizes and an organic solvent is removed. Next, it changes into the condition of having pulled out the lead wire for anode plates which consists the impalpable powder of this valve action metal of valve action metals, such as a tantalum, and presses into the configuration of a square shape, a cylindrical shape, etc. with a press etc. After compression molding, in the ambient atmosphere of the vacuum middle class, grade heating is carried out for 15 - 60 minutes, and it sinters by about 1800-2200-degree C high temperature, and a sintered compact 1 is formed as shown in drawing (1). The impurity in powder is also evaporated at the time of this sintering.

[0008] The disc-like electric insulating plate 3 which becomes the origin of the lead wire 2 for anode plates from Teflon, silicone rubber, silicone resin, etc. is arranged after sintering. This electric insulating plate 3 has thickness thinner than 0.2mm, and its thickness of about 0.1mm is preferably good. That is, a capacitor can be miniaturized, when the one where the thickness of an electric insulating plate 3 is thinner can enlarge the dimension of a sintered compact, and can increase capacity and fixes capacity, without changing the dimension of the whole capacitor.

[0009] And the tip of the lead wire 2 for anode plates currently pulled out from this sintered compact 1 is welded to the metal plates 4, such as aluminum and stainless steel, as shown in drawing 1 (b). Two or more sintered compacts 1 are attached in a metal plate 4 for the increase in efficiency of an activity. and this condition -- a sintered compact 1 -- formation of a nitric acid, a phosphoric acid, etc. -- while being immersed to predetermined level by viewing etc. into liquid, chemical conversion of the direct current voltage according to rated voltage is impressed and carried out to this. This chemical conversion generates an oxide film at about 16A/about V rate, and finally the oxide film 5 with a thickness of about 200-6000Å is formed as shown in drawing 1 (Ha).

[0010] After forming an oxide film 5, the conductive polymer layer 6 is formed in the front face as shown in drawing 1 (d). This conductive polymer layer 6 is formed by the electrolytic polymerization method or the chemistry oxidation-polymerization method. And in the case of the latter approach, it forms as follows, for example. That is, the 1st approach sinks into a sintered compact 1 the solution which dissolved first the mixture of an oxidizer or an oxidizer, and the

matter that gives the dopant which consists of an acid compound or a salt compound in the suitable solvent. Then, when the solution of an oxidizer is used, the solution which consists of mixture of a monomer and the matter which gives the dopant which consists of an acid compound or a salt compound is infiltrated, the chemistry oxidation-polymerization reaction of the monomer is carried out, a dopant is combined, and conductivity is given. Moreover, when the mixed solution of an oxidizer and matter, such as an acid compound, is used, one of the mixed solutions of a monomer or a monomer, and the matter that gives the dopant of an acid compound or a salt compound is sunk in, the chemistry oxidation-polymerization reaction of the monomer is carried out, a dopant is combined, and conductivity is given. And the count loop of predetermined of these sinking-in processings is carried out, and it is made predetermined thickness. Then, desiccation processing is carried out. Moreover, the 2nd approach sinks the solution of the mixture of a monomer or a monomer, and an acid compound and a salt compound into a sintered compact 1 first. Then, conductivity is given, while sinking in and carrying out the chemistry oxidation-polymerization reaction of the solution of the mixture of an oxidizer and the matter which gives the dopant of an acid compound or a salt compound, when the solution of a monomer is used. Moreover, when mixed solutions, such as a monomer and an acid compound, are used, the mixed solution of an oxidizer or an oxidizer, an acid compound, etc. is sunk in, the chemistry oxidation-polymerization reaction of the monomer is carried out, and conductivity is given. And the count loop of predetermined of these sinking-in processings is carried out, and it is made predetermined thickness. Then, desiccation processing is carried out. Furthermore, the 3rd approach sinks into a sintered compact 1 a monomer, the matter which gives the dopant of an acid compound or a salt compound, and the solution which dissolved the mixture of an oxidizer in the suitable solvent, carries out the chemistry oxidation pile reaction of the monomer, and gives conductivity. And the count loop of predetermined of this sinking-in processing is carried out, and it is made predetermined thickness. Then, desiccation processing is carried out.

[0011] In addition, an oxidizer is made into the concentration of 0.1 - 1.0 mol/l extent using a potassium dichromate, a sodium dichromate, pel oxo-disulfuric acid ammonium, a hydrogen peroxide, ferric chloride, potassium permanganate, a manganese dioxide, a lead dioxide, etc.

[0012] And a sulfonic-acid compound, a carboxylic-acid compound, a phosphoric-acid compound, etc. are used for the acid compound used as matter which gives a dopant. Especially as a sulfonic-acid compound, a dissociation constant is almost the same as that of a naphthalene sulfonic acid or its derivative, or considers as the matter with the anion of a dopant smaller than the anion of a naphthalene sulfonic acid or its derivative smaller. As such a sulfonic-acid compound, acids, such as for example, sulfone isophthalic acid, a sulfo succinic acid, methansulfonic acid, phenolsulfonic acid, a sulfosalicylic acid, benzenesulfonic acid, a benzene disulfon acid, alkylbenzene sulfonic acid and its derivative, a camphor sulfonic acid, a sulfone acetic acid, and a diphenol sulfonic acid, are used. Concentration of this acid compound is made into 0.05 - 1.0 mol/l extent. Moreover, the ammonium salt and sodium salt of the aforementioned acid compound, and potassium salt are used for the salt compound used as matter which gives a dopant. That is, in the case of a sulfonic-acid compound, salts, such as sulfoisophtharate ammonium, sulfo succinic-acid ammonium, methansulfonic acid ammonium, phenolsulfonic acid ammonium, sulfosalicylic-acid ammonium, benzenesulfonic acid ammonium, benzene disulfon acid ammonium, alkylbenzene-sulfonic-acid ammonium and its derivative, camphor sulfonic-acid ammonium, sulfone ammonium acetate, and diphenol sulfonic-acid ammonium, are used as an aluminum salt. And as sodium salt, salts, such as sulfoisophtharate sodium, the sulfo sodium succinate, methansulfonic acid sodium, the sodium phenolsulfonate, sodium

sulfosalicylate, benzenesulfonic acid sodium, benzene disulfon acid sodium, alkyl benzene sodium sulfonate and its derivative, camphor sulfonic-acid sodium, sulfone sodium acetate, and diphenol sulfonic-acid sodium, are used. Furthermore, as potassium salt, salts, such as a sulfoisophtharate potassium, the sulfo potassium succinate and a methansulfonic acid potassium, a phenolsulfonic acid potassium, a sulfosalicylic-acid potassium, a benzenesulfonic acid potassium, a benzene disulfon acid potassium, an alkylbenzene-sulfonic-acid potassium and its derivative, a camphor sulfonic-acid potassium, sulfone potassium acetate, a sulfo aniline, and a diphenol sulfonic-acid potassium, are used. And concentration of the compound of these ammonium salt and sodium salt, and potassium salt is also made into 0.05 - 1.0 mol/l extent. Moreover, in order to raise the solubility of a salt compound and to lower the concentration in liquid, a hydrochloric acid, a sulfuric acid, etc. may be added.

[0013] Furthermore, it is made the concentration of 0.1 - 1.0 mol/l extent, for example, using acetylene, PARAFENIREN and a pyrrole, vinylene, phenylene, an aniline, a thiophene, an imidazole, a thiazole, a furan, etc. as a monomer.

[0014] Next, a graphite solution is applied to the front face of the conductive polymer layer 6, and the graphite layer 7 is formed in it as shown in drawing 1 (e). After forming the graphite layer 7, a silver paste is applied to this front face, a silver layer 8 is formed as shown in drawing 1 (passing), together with the graphite layer 7, it considers as catholyte 9, and a capacitor element 10 is formed. After forming a silver layer 8, while connecting the leadframe-like cathode terminal 12 to a silver layer 8 with the electroconductive glue 11, such as a silver conductivity paste, as shown in drawing 1 (g), the lead wire 2 for anode plates is connected to the leadframe-like anode terminal 13. And the sheathing 14 which consists of resin with the resin mold method, a resin dip method, etc. is formed as shown in drawing 1 (h).

[0015] After forming sheathing 12, the electrical potential difference more than rated voltage is impressed at a room temperature, and 1st aging processing is carried out. In addition, several ten capacitor elements are usually connected to the leadframe. Therefore, it is more desirable for the 1st aging processing to connect one DC power supply to the leadframe of one sheet, and to perform it for every leadframe. That is, one DC power supply are connected to the leadframe of two or more sheets, an electrical potential difference is impressed to each capacitor element, if aging processing is carried out, several 100 or more capacitor elements will be aged to coincidence, the current capacity of DC power supply will run short, it will also happen that each capacitor element does not carry out a pressure up to a predetermined electrical potential difference, and poor aging will be produced. Moreover, when current capacity of DC power supply is enlarged according to the number of capacitor elements, it comes to be able to carry out the pressure up of the electrical potential difference of a capacitor element to a predetermined value. However, the rush current when impressing an electrical potential difference to each capacitor element in this case may become large, the leakage current may become large more, and the big capacitor element of the leakage current may be destroyed. And the time amount for about several seconds is sufficient as this 1st aging processing, and its effectiveness of falling the leakage current as a long duration line hardly improves. After the 1st aging processing, the electrical potential difference more than rated voltage is impressed into the ambient atmosphere of high temperature (for example, 85 degrees C), and 2nd aging processing is performed. In addition, the range of temperature of 85-125 degrees C is desirable, the range which is 85-105 degrees C is especially desirable, and the effectiveness of falling the leakage current becomes more remarkable. Moreover, if the effectiveness of time amount of about several hours being desirable and decreasing the leakage current for a short time is low and it carries out for a long

time, a leakage current property will fall conversely.

[0016] And after the 2nd aging processing, foaming of a cathode terminal 12 and the anode terminal 13 is carried out, and a solid electrolytic capacitor 15 is manufactured as shown in drawing 1 (Li).

[0017]

[Example] Next, the example of this invention is explained. First, press compression molding of the powder which mixed the binder to the impalpable powder of a tantalum is carried out at a square shape. In this case, the end of the lead wire for anode plates made from a tantalum is inserted into powder, and it is made the structure which pulled out the other end. After compression molding, it sinters in a vacuum and the sintered compact of a 1.62mmx3.25mmx3.80mm angle is formed. Next, it is immersed into a nitric-acid solution, chemical conversion of this sintered compact is carried out by formation voltage 25V, and an oxide film is formed in this. The layer of a conductive polymer which consists of a poly aniline is formed by the chemistry oxidation-polymerization method on the surface of an oxide film after forming an oxide film. Under the present circumstances, since it is necessary to carry out a laminating also to the periphery section by predetermined thickness, and to form a conductive polymer layer while filling up the interior of a sintered compact with the poly aniline, chemistry oxidation-polymerization processing is repeated. It is immersed into [ after forming a conductive polymer layer ] a graphite solution, and a graphite layer is formed. And after forming a graphite layer, a silver paste is applied and a silver larer is formed. After forming a silver larer, while connecting a silver larer to the cathode terminal area of a leadframe with electroconductive glue, the lead wire for anode plates is connected to the anode plate terminal area of a leadframe by resistance welding. And by the same approach, 30 capacitor elements after silver larer formation are connected to the leadframe of one sheet. Then, sheathing which consists of an epoxy resin by the transfer mold method is formed. A part of leadframe is cut after forming sheathing. After cutting, at a room temperature, a sink and the electrical potential difference of 13V are impressed for a maximum of 1 A for 4 seconds using one DC power supply to the leadframe of one sheet, and 1st aging processing is performed. and the inside of an ambient atmosphere with an after [ this 1st aging processing ] and a temperature of 85 degrees C -- setting -- the electrical potential difference of 11V -- 6-hour continuation impression -- carrying out -- the 2nd aging processing -- it carries out. The remainder of a leadframe is cut after this 2nd aging processing, foaming of a cathode terminal and the anode terminal is carried out, and a tantalum chip mold solid-state electrolytic capacitor (rated 6.3V and 150 micro F) is built. In addition, the applied voltage at the time of the 1st aging processing and the 2nd aging processing has increased about 2.06 times of rated voltage, and about 1.75 times respectively.

[0018] And about the tantalum solid electrolytic capacitor manufactured by the approach of this example, each leakage current after sheathing formation, the 1st aging processing, and the 2nd aging processing is measured, and it is shown in drawing 2 .

[0019] Moreover, about the tantalum solid electrolytic capacitor manufactured by the approach of the example of a comparison, the leakage current after aging processing is measured and it is similarly shown in drawing 1 . In addition, this example of a comparison omits the 1st aging processing, uses one DC power supply for 40-sheet coincidence for the leadframe which connected 30 capacitor elements to one sheet into the ambient atmosphere with a temperature of 85 degrees C, and makes the current of a maximum of 5 A the same approach as an example except impressing a sink and the electrical potential difference of 11V for 6 hours, and carrying out aging processing.

[0020] And let the leakage current be the value 5 seconds after impressing rated voltage. Moreover, the number of samples is respectively made into 60 pieces.

[0021] As for the leakage current (average value) of an example, the 46microA and 2nd aging processing back is set [ the sheathing formation back ] to 25microA by the 684microA and 1st aging processing back a passage clear from the measurement result of drawing 2 . On the other hand, the leakage current (average value) of the example of a comparison is set to 52microA after aging processing. That is, if the direction depended on the former approach compares by the leakage current after the 2nd aging processing, it has the 1/2 or less latter magnitude. Moreover, the former leakage current serves as the range of 13-41microA after the 2nd aging processing, and the latter leakage current is set to 19-1995microA, and former one has less variation than the latter, and has not generated the poor leakage current. In the case of the latter, this is because the rush current at the time of aging processing is large.

[0022]

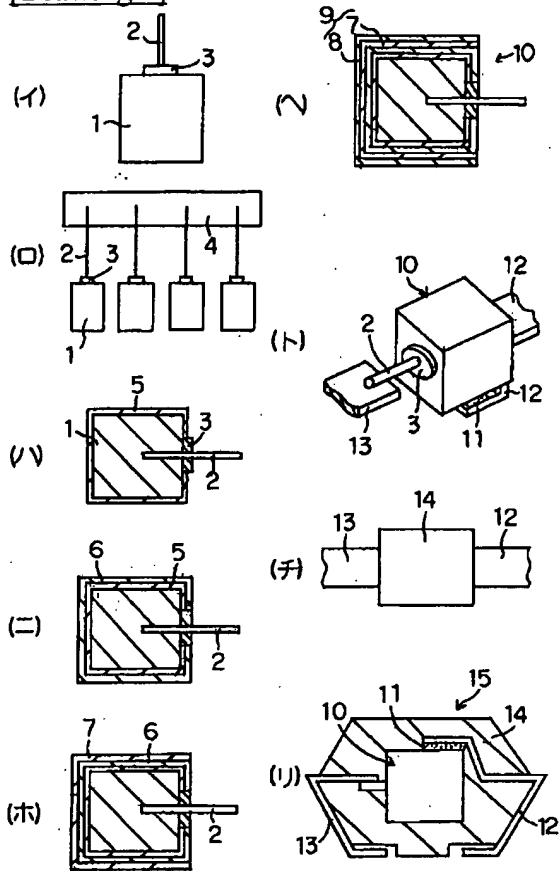
[Effect of the Invention] According to the manufacture approach of this invention the above passage, an oxide film is formed in the sintered compact which consists of powder of a valve action metal. In the manufacture approach of the solid electrolytic capacitor which forms sheathing which becomes the capacitor element which carried out the laminating of a conductive polymer layer and the catholyte to this oxide film one by one from resin, and carries out aging processing after that The electrical potential difference more than rated voltage is impressed at a room temperature, 1st aging processing is carried out, after that, since the electrical potential difference more than rated voltage is impressed in the ambient atmosphere of high temperature and 2nd aging processing is carried out, a leakage current property can be improved, a defect can be reduced and the solid electrolytic capacitor which can improve dependability is obtained.

---

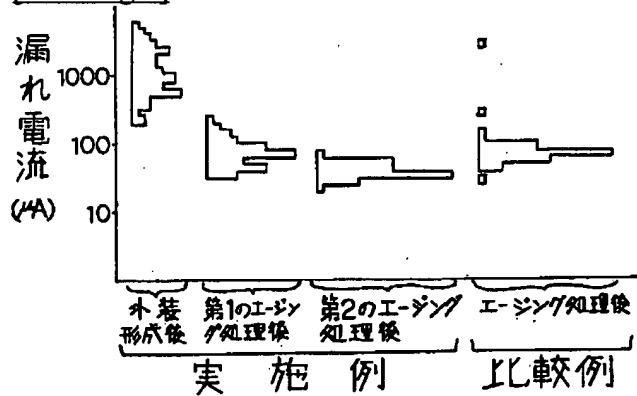
## DRAWINGS

---

[Drawing 1]



[Drawing 2]



## CLAIMS

### [Claim(s)]

[Claim 1] The manufacture approach of the solid electrolytic capacitor which impresses the electrical potential difference more than rated voltage in ordinary temperature, carries out the 1st aging processing, impresses the electrical potential difference more than rated voltage in the ambient atmosphere of high temperature after that, and is characterized by the 2nd thing do for

aging processing in the manufacture approach of the solid electrolytic capacitor which forms the oxide film in the sintered compact which consists of a valve-action metal, forms sheathing which becomes the capacitor element which carried out the laminating of a conductive-polymer layer and the catholyte to this oxide film one by one from resin, and carries out aging processing after that.